

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 293/00, C09D 153/00, 5/03		A1	(11) International Publication Number: WO 99/62978 (43) International Publication Date: 9 December 1999 (09.12.99)
<p>(21) International Application Number: PCT/NL99/00340</p> <p>(22) International Filing Date: 1 June 1999 (01.06.99)</p> <p>(30) Priority Data: 98201851.7 4 June 1998 (04.06.98) EP 98203137.9 18 September 1998 (18.09.98) EP</p> <p>(71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): RIETBERG, Johan [NL/NL]; Penningkruidweg 36, NL-8042 NR Zwolle (NL). UDDING, Jan, Henderikus [NL/NL]; Stadhoudelaan 59, NL-8042 AB Zwolle (NL). UDDING-LOUWRIER, Saskia [NL/NL]; Stadhoudelaan 59, NL-8042 AB Zwolle (NL).</p> <p>(74) Agent: SCHMEETZ, Marcel, Max, Hubertina, Johanna; Octroibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. With amended claims.</p>	

(54) Title: POWDER-PAINT BINDER COMPOSITION

(57) Abstract

The invention relates to a powder paint composition comprising an A-B-C block polymer formulated from an ethylenically unsaturated monomer, said A block and said C block being terminally disposed and said B block being interposed between said A block and said C block; said A block and said C block having cross-linkable functional groups, said B block being essentially free of reactive functional groups.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PC.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

POWDER-PAINT BINDER COMPOSITION

5 The invention relates to a powder-paint binder composition comprising a polymer based on an ethylenically unsaturated monomer and optionally a crosslinker.

10 Polymers comprising ethylenically unsaturated monomer units, such as for example polyacrylates, can be obtained through radical polymerization, in which functional groups are randomly distributed across the polymer. Such polymers are described in Paint and Surface Coatings (R. Lambourne, 15 pp. 68-74, 1987, Ellis Horwood Limited), the complete disclosure of which is incorporated herein by reference. However powder coatings obtained after curing of a powder paint composition containing a binder composition which includes a polyacrylate and a 20 crosslinker are known to be too brittle and too sensitive to damage upon exposure to solvents.

25 It is the object of the present invention to provide a curable powder paint binder composition comprising an ethylenically unsaturated monomer based polymer, which results in a powder coating exhibiting good mechanical properties and a superior resistance to chemicals.

30 The invention is characterized in that the powder paint binder composition comprises an A-B-C block polymer formulated from an ethylenically unsaturated monomer, said A block and said C block being terminally disposed and said B block being

interposed between said A block and said C block; said A block and said C block having crosslinkable functional groups, said B block being essentially free of reactive functional groups.

5 The functional groups are located at the end blocks A and C of the polymer. The combined weight percent of the end blocks A and C is generally less than 30 wt.% of the total weight of the A-B-C- block copolymer.

10 After curing of the powder paint composition comprising the binder composition according to the invention the powder coating has a good resistance to yellowing and to weather influences, and exhibits good flow behaviour, good storage stability, 15 good resistance to chemicals, a high gloss, high scratch resistance and good mechanical properties.

The invention also relates to the A-B-C block polymer having functional end groups.

According to a preferred embodiment of the 20 invention the polymer has been obtained through controlled radical polymerization in the presence of an initiator and a metal complex or a metal-containing compound.

The method of producing the A-B-C block 25 polymer for use in a curable powder-paint binder composition, can comprise the steps of:

- a) providing a mixture, said mixture comprising an effective amount of an initiator and an effective amount of a catalyst;
- 30 b) adding a first functionalized monomer to said mixture, said first functionalized monomer comprising for example an ethylenically unsaturated mono- or dicarboxylic acid derivative;

c) polymerizing said first functionalized monomer at a suitable temperature and pressure to effectively polymerize said first functionalized monomer to form A block of said A-B-C block polymer;

5 d) adding a non-functionalized monomer to said mixture, said non-functionalized monomer having essentially no reactive functional groups which are crosslinkable to said first functionalized monomer, and polymerizing said non-functionalized monomer to form B block of said

10 A-B-C block polymer;

e) adding a second functionalized monomer to said mixture, said second functionalized monomer having no functional groups which are crosslinkable to said non-functionalized monomer, and polymerizing said second

15 functionalized monomer to obtain C block of said A-B-C block polymer,

thereby obtaining said A-B-C block polymer, wherein said A block and said C block of said A-B-C block polymer are terminally disposed and said B block is

20 interposed between said A block and said C block, said B block being essentially free of reactive functional groups which are crosslinkable with those on said A block and said C block.

The location of the functional groups in

25 the end blocks A and C is contrary to the random distribution of functional units across the whole of poly(meth)acrylates conventionally used in powder-paint binder compositions.

The block B contains essentially no

30 reactive or crosslinkable functional groups. Block B may however include various monomer units such as, for example, alkyl(meth)acrylates and styrene.

Examples of suitable functional monomers in blocks A and C include (meth)acrylic acid, (meth)acrylic acid esters, glycidyl (meth)acrylate and hydroxyethyl (meth)acrylate. The functional monomers in 5 A and C may be the same or different. Preferably, the monomers in blocks A and C are epoxy, carboxyl and hydroxyl groups.

Suitable ethylenically unsaturated monomers include, for example, styrene, acrylonitrile and 10 ethylenically unsaturated mono- or dicarboxylic acid derivatives. These derivatives include preferably esters, of (C₃-C₆) monoethylenically unsaturated monocarboxylic acids, such as for example (meth)acrylic acid and crotonic acid, and (C₄-C₆) monoethylenically 15 unsaturated dicarboxylic acids such as, for example, maleic acid, maleic anhydride, itaconic acid and fumaric acid.

(Meth)acrylic acid ester and styrene are preferred.

20 Suitable (meth)acrylic acid derivatives include, for example, (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, propyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, benzyl (meth)acrylate and hydroxyalkyl (meth)acrylates such as 25 hydroxyethyl and hydroxypropyl (meth)acrylate and/or glycidyl esters or glycidyl ethers of alkyl (meth)acrylates.

30 Acrylate-based polymers containing different reactive functional groups can be used in the binder composition according to the invention.

Examples of suitable functional groups are carboxyl groups, epoxy groups, anhydride groups, hydroxyl groups, acetoacetonate groups and combinations thereof.

5 The degree of branching of the polymer is generally between 2 and 6. Branching refers to the extensions of the polymer chain(s) attached to the polymer backbone.

10 The molecular weight (Mn) of the polymer is usually higher than 800 and is preferably higher than 1500. To obtain good flow behaviour at temperatures between 100°C and 200°C, the molecular weight (Mn) is usually lower than about 10,000 and preferably lower than about 7000.

15 The polydispersity is generally lower than 2 and usually lies between 1.1 and 1.8. The polydispersity (Mw/Mn) has been determined with the aid of size exclusion chromatography using a viscosimeter detector.

20 The Tg of the polyacrylate is generally between about 30°C and about 120°C. Relatively larger amounts of crosslinker can be used in the binder composition if the Tg lies at the upper limit of this range. To obtain an optimum storage stability, the Tg 25 is preferably higher than 50°C. With a view to the processing of the polymer the Tg is preferably lower than 100°C.

The viscosity of the polyacrylate is generally between 100 and 8000 dPas (measured at 160°C 30 using a Rheometric Plate-Plate).

The polymerization according to the invention generally takes place at temperatures between 60°C and 180°C and preferably between 80°C and 170°C. The

pressure is generally between 1 and 10 atmospheres. The polymerization is carried out under an inert atmosphere.

Suitable examples of initiators used in 5 producing the A-B-C block polymer include halogen containing compounds, for example, α -halo-substituted carboxylic (C_1-C_6)alkyl esters.

Suitable halogen atoms e.g. halo- 10 subsituents are for example chloro and bromo. Examples of such initiators are α -(mono-, di-, or tri-)chloro or bromo acetic methyl ester, α -(mono- or di-)chloro- or bromo propionic methyl ester, α -chloro or bromo butyric methyl ester and α -chloro or bromo malonic dimethyl ester.

15 The initiators may also be multi-functional, such as, for example, 4-vinyl benzyl chloride, α,α' -dibromo-p-xylene, α,α -dichloro-p-xylene, 2,4-mesitylene disulphonyl chloride, tosyl chloride, mesylchloride, 1,3,5-tris(bromomethyl)benzene, tetrakis 20 (bromomethyl)benzene, hexakis (bromomethyl)-benzene, 1,4-dibromo-2-butene, and esters of the aforementioned α -halogen-substituted carboxylic acids with diols and polyols such as, for example, the tri(dichloroacetic acid) ester of trimethylol propane, the di(alpha-bromo propionic acid) ester of ethylene glycol and the 25 di(dichloroacetic acid) ester of ethylene glycol.

Preferably dichloro methyl acetate is used as the initiator.

30 The metals may be present in a compound with a covalent or ionic bond or in a complex with a coordination bond.

The metal containing compound or the metal complex may act as a catalyst.

Suitable metallic elements are Cu, Fe, Ag, Ti, W, U, Al, Mo, Pd, Ru, Rh and Ni.

5 Preferably Cu, Fe, Ru and Ni are used.

Preferably, the catalyst is a metal complex based on one or more metal ions or salts with exchangeable counterions and ligands.

10 The number of counterions lies between 0 and 6 and preferably between 1 and 4. In the case of tetravalent metals it is possible to use, for example, four monovalent counterions, two divalent counterions or a combination of a trivalent and a monovalent counterion. Preferably four monovalent counterions are 15 used.

In the case of trivalent metals the number of counterions is between 1 and 3. Preferably three monovalent counterions are used.

20 Examples of suitable counterions include halides, preferably chloride and bromide, (C_1-C_{20}) alkoxides, preferably (C_1-C_8) alkoxide, (C_2-C_{20}) carboxylates, preferably (C_2-C_8) carboxylates, enolates, preferably of 2,4-pentanedione (acetylacetones) and alkyl esters of malonic acid and acetyl acetic acid, 25 phenolates, naphthenates, cresylates and mixtures of said counterions.

Suitable ligands include, for example, (substituted) bipyridines, pyridines, bi- and tridentate amines, mono-, bi- and tridentate 30 phosphines, imines and nitriles.

Examples of suitable bipyridines include 2,2'-bipyridine and 4,4'-dialkyl-2,2'-bipyridine.

- 8 -

Examples of amines are tetramethylethylene diamine (TMEDA), tetramethylpropylene diamine and pentamethylene diethylene triamine.

Suitable phosphines include for example 5 triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, R(+)-2,2'-bis(diphenylphosphino)1,1-binaphthyl, S(-)2,2'-bis(diphenylphosphino)1,1-binaphthyl, PPh₃, and 1,2-bis(dimethylphosphino)ethene.

10 Suitable nitriles include for example acetonitrile and succinonitrile.

Suitable pyridines include for example pyridine, alkylpyridine, 2,2'-bipyridine, 4,4'dialkyl-2,2'-bipyridine, 2-pyridyl acetonitrile and 2,2':6',2'-terpyridine.

Suitable imines can be obtained by the reaction of salicylaldehyde with a compound containing nitrogen atoms. Preferably, the nitrogen compound is a polyamine such as, for example, ethylenediamine, cis-20 1,2-cyclohexanediamine, trans-1,2-cyclohexanediamine (racemic), [S,S]-trans-1,2-cyclohexanediamine, [R,R]-trans-1,2-cyclohexanediamine, N-methylbisethylene-triamine, triethylenetetraamine, 3,3'-diamino-N-methyldipropylamine, 1,2-phenylenediamine, 1,1,2,2,-25 tetramethylethylenediamine and propylene imine dendrimers.

It is also possible to use, for example, substituted o-hydroxybenzaldehydes instead of salicylaldehyde.

30 Suitable substituents include for example alkyl, aryl, halogen, nitrile, nitroxyl, dialkylphosphino, diarylphosphino, pyridyl, aminoalkyl, aminoaryl, carboxyl, hydroxyl and carbonyl groups.

Optionally a small amount, for example between 0.001 and 2 mol.%, of metal salts can be added during the production of the A-B-C-block polymer. Examples of such salts include CuCl₂, CuBr₂ or FeCl₃.

5 The catalysts can also be applied to a carrier such as, for example, silica.

The controlled living radical polymerization may take place by bulk polymerization or by solvent polymerization in the presence of solvents 10 such as, for example, toluene, acetonitrile, xylene, 1,2-dichloroethane, tert-butyl benzene, methyl ethyl ketone, dimethyl formamide, dimethyl sulphoxide, mesitylene, butyl acetate and benzene.

Controlled living radical polymerizations 15 are described in J. Am. Chem. Soc. 1997, 119, 674-680, and in Macromolecules, 1995, 28, 7901-7910, the complete reference of which is incorporated herein by means of reference.

A preferred embodiment of producing the A- 20 B-C block polymer comprises adding the functionalized monomer or a mixture of a functionalized monomer and a non-functionalized monomer to a mixture, consisting of the catalyst and the initiator, in a solvent. Suitable solvents include, for example, toluene, butyl acetate 25 and methyl isobutyl ketone.

The amount of initiator used is between about 0.01 and about 10 mol.% relative to the monomers. The amount of catalyst used is between about 0.001 and about 10 mol.% relative to the monomers.

30 After the percentage of conversion of the functionalized monomer in block A has passed, for example, 90%, non-functionalized monomer B can be added.

- 10 -

After the percentage of conversion of the total amount of monomers A + B has passed for example, 85% functionalized monomer C can be added.

Block A can also be formed by initiator 5 with functional groups such as, for example, 2-bromo-2-methyl-hydroxy ethylpropionate, 2-bromo-hydroxy ethylpropionate, hydroxyethyl dichloroacetate, trichloroethanol, trichlorobutanol, trichloropropanol, tribromoethanol, tribromopropanol, and/or 10 tribromobutanol.

Block C can also be formed by addition of a functional alkene compound. Suitable alkene compounds include allylalcohol, methylbutenol and allylglycidyl-ether.

15 On completion of the polymerization metal salts and/or ligands can be removed via filtration over silica or washing with water.

A thermosetting powder-paint binder composition can contain more than 50 wt.% polymer and 20 less than 50 wt.% crosslinker. In general more than 2 wt.% crosslinker is used although the use of less than 15 wt.% crosslinker is preferred. These amounts are defined as wt.% relative to the total amount the combined weight of the of polymer and crosslinker.

25 The crosslinker has to be capable of reacting with the functional groups being present in blocks A and C of the A-B-C block polymer.

Examples of suitable crosslinkers include 30 triglycidyl isocyanurate (TGIC), polybisphenol-A epoxides, compounds containing (blocked) isocyanate groups, compounds containing β -hydroxyalkylamide groups, amino resins, crosslinkers containing acid groups and crosslinkers (as described in EP-A-600546)

- 11 -

comprising at least one aliphatic branched or linear chain with an epoxy functionality containing 5-26 carbon atoms such as, for example, epoxidized oils.

The polyacrylates obtained according to the present process also offer the possibility of using a "full-acrylic" system. In this case an oligomer or polymer containing acrylate groups takes over the function of the crosslinker. As an example of such a system an acid-functional polyacrylate obtained via the living polymerization described above can be combined with a state of the art glycidyl methacrylate copolymer.

The curing reaction between the polymer and the crosslinker which results in the ultimate cured coating will be a function of the polymer and the crosslinker which is selected. This curing reaction can be effectuated, if desired, in the presence of an effective amount of catalyst. With the binder composition according to the invention it is possible to choose the desired curing time by adjusting the type and amounts of catalyst used and/or the curing agent. The importance of the ratio of the polymer and the crosslinker described above and of the amount of catalyst is explained in Misev, Powder Coatings, Chemistry and Technology pp. 174-223 (1991, John Wiley), the complete disclosure of which is incorporated herein by reference.

In addition to the aforementioned A-B-C triblock copolymers, A-B-C polymers with several branches that are linked to one another via one or more branching points can also be made. The multifunctional initiators already described above can be used to this end during the preparation. These materials, too, may

consist of one or more polymer blocks each consisting of various monomers. On account of their improved flow behaviour, the materials thus formed can be used as viscosity regulators in, for example, coatings and 5 polymer mixtures. These mixtures may contain polymers based on monomers that can be cured with the aid of radicals such as, for example, styrene acrylonitrile, styrene or methyl (meth)acrylate. In addition, the relatively large number of terminal groups can be used 10 to provide materials with improved adhesion properties. These materials moreover show improved UV and melting resistance in comparison with linear materials.

The invention is directed to a powder paint binder composition containing an A-B-C block polymer 15 formulated from an ethylenically unsaturated monomer, said A block and said C block being terminally disposed and said B block being interposed between said A block and said C block; said A block and said C block having functional groups, said B block being essentially free 20 of reactive functional groups and wherein at least one of the functional groups of the A block and the C block is modified into a functional group with a different chemical reactivity.

By selecting a specific reagent or a type 25 of reagent it is possible, to obtain a polymer which has, with respect to the starting A-B-C polymer, at least one other desired functional group having a different chemical reactivity than the starting functional group. Consequently a broad range of 30 polymers and a broad range of crosslinkers can be combined to obtain powder paint formulations with desired properties.

In Table I a survey of examples of possible modifications is given:

Table I

Functional group in A and/or C block of A-B-C block polymer	Reagent or type of reagent	Resulting functional group in modified A-B-C block polymer
hydroxyl	anhydride, diacid	carboxylic acid
	alkylacetooacetate	acetooacetate
	NCO functional alkoxy silane	alkoxy silane
	polyisocyanate and hydroxylvinyl ether or aminovinyl ether	vinyl ether
	polyisocyanate and allylalcohol or propenol	allyl or propenyl
	polyisocyanate and hydroxy (meth)acrylate	(meth)acrylate
	itaconic anhydride or itaconic acid	itaconate
	maleic anhydride, maleic acid or fumaric acid	maleate or fumarate
	alkoxy methyl (meth)acrylamide	acrylamide
	(meth)acrylic acid, (meth)acrylic acidalkylester, (meth)acrylic anhydride	(meth)acrylate
carboxylic acid	ethylene oxide, propylene oxide, ethylene carbonate, propylene carbonate	hydroxy
	epoxy functional alkoxy silane	alkoxy silane
	hydroxy amine	oxazoline
	amine	amide
	glycidyl (meth)acrylate	(meth)acrylate
epoxy	CO ₂	carbonate
	(meth)acrylic acid	(meth)acrylate

Regarding Table I, the modification of the starting A-B-C block polymer can, for example, take place by reaction of this A-B-C block polymer and a compound comprising an ethylenically unsaturated group, 5 an acid group, an hydroxy group, an isocyanate group, an acetoacetate group, an epoxide group, a vinylidene group or a fatty acid group.

Said modification with an ethylenically unsaturated groups will result in a polymer having, for 10 example, (meth)acrylate, vinylidene, fumaric or maleic end groups. The selection of the ethylenically unsaturated groups depends on the functionality in blocks A and C.

Furthermore, the present invention can 15 result, for example, in that a polymer having carboxyl groups in A or C may be modified with glycidyl (meth)acrylate, a polymer having epoxy groups in A or C may be modified with (meth)acrylic acid and a polymer having hydroxyl groups in A or C may be modified with a 20 polyisocyanate and a hydroxyvinylidene or hydroxy (meth)acrylate or allylalcohol.

A polymer containing hydroxylgroups may 25 also be modified with an unsaturated carboxylic acid such as for example fumaric acid or maleic acid anhydride and may also be functionalised with a saturated anhydride to an acid.

At the end blocks A and C of the A-B-C polymer functional groups are located. Examples of suitable functional groups are carboxyl groups, epoxy groups, anhydride groups, hydroxyl groups, 30 acetoacetate groups and combinations thereof.

The combined weight percent of the end blocks A and C is generally less than 30 wt.% of the total weight of the A-B-C block copolymer.

The A-B-C polymer can be obtained through 5 controlled radical polymerization in the presence of an initiator and a metal complex or a metal-containing compound, after which the modification takes place in a second step.

A method of producing this functionalised 10 A-B-C block polymer can comprise the steps of:

- providing a mixture, said mixture comprising an effective amount of an initiator and an effective amount of a catalyst;
- adding a first functionalized monomer to said 15 mixture, said first functionalized monomer comprising for example an ethylenically unsaturated mono- or dicarboxylic acid derivative;
- polymerizing said first functionalized monomer at a suitable temperature and pressure to effectively 20 polymerize said first functionalized monomer to form A block of said A-B-C block polymer;
- adding a non-functionalized monomer to said mixture, said non-functionalized monomer having essentially no reactive functional groups which are 25 crosslinkable to said first functionalized monomer, and polymerising said non-functionalized monomer to form B block of said A-B-C block polymer;
- adding a functionalised alkene compound to said mixture or adding a second functionalized monomer 30 to said mixture, said second functionalized monomer having functional groups which are not crosslinkable to said non-functionalized monomer, and polymerizing said second functionalized monomer

to obtain C block of said A-B-C block polymer, thereby obtaining said A-B-C block polymer, wherein said A block and said C block of said A-B-C block polymer are terminally disposed and said B block is interposed between said A block and said C block, said B block being essentially free of reactive functional groups which are crosslinkable with those on said A block and said C block and

5 f) functionalising the A-B-C blockpolymer.

10 A method of producing the functionalised A-B-C block polymer can, for example, also comprise the steps of:

15 a) providing a mixture, comprising a functionalized initiator, a catalyst and a non-functionalized monomer, said non-functionalized monomer having essentially no reactive functional groups which are crosslinkable to said functionalized initiator, and polymerizing said non-functionalized monomer to form the A and B blocks of said A-B-C block

20 polymer;

b) adding a functional alkene compound to said initiator or adding a functionalized monomer to said mixture, said functionalized monomer having functional groups which are not crosslinkable to said non-functionalized monomer, and polymerizing said functionalized monomer to obtain C block of said A-B-C block polymer, thereby obtaining said A-B-C block polymer, wherein said A block and said C block of said A-B-C block polymer are terminally

25 disposed and said B block is interposed between said A block and said C block, said B block being essentially free of reactive functional groups

30

which are crosslinkable with those on said A block and said C block and

c) functionalising the A-B-C blockpolymer.

As shown in Table I the A-B-C blockpolymer 5 can be functionalised with different components. The reaction conditions and the reagents depend on the selection of the reaction components and the intended application.

The molecular weight (Mn) of the modified 10 polymer is usually higher than 400 and is preferably higher than 600. To obtain good flow behaviour at temperatures between 100°C and 200°C, the molecular weight (Mn) is usually lower than about 10,000 and preferably lower than about 7000.

15 The Tg of the modified A-B-C polymer, for example a polyacrylate, is generally between about 30°C and about 120°C. To obtain an optimum storage stability, the Tg is preferably higher than 50°C. With a view to the processing of the polymer the Tg is preferably 20 lower than 100°C.

The modified polymer can be applied in a powder paint composition as a polymer, as a crosslinker and as the binder system.

In case the polymer acts as a crosslinker a 25 suitable polymer has to be selected, in case the polymer acts as the polymer a suitable crosslinker has to be selected and in case the polymer acts as the binder system there is no need for a further polymer or crosslinker.

30 Preferably a carboxylic acid functional polymer, obtained by modification of an hydroxy functional A-B-C block polymer with an anhydride or diacid, may be crosslinked with triglycidyl

isocyanurate (TGIC), polybisphenol-A epoxides, compounds containing (blocked) isocyanate groups, compounds containing β -hydroxyalkylamide groups, amino resins, crosslinkers containing acid groups and 5 crosslinkers (as described in EP-A-600546) comprising at least one aliphatic branched or linear chain with an epoxy functionality containing 5-26 carbon atoms such as, for example, epoxidized oils.

A binder composition according to the 10 invention yields a good coating after thermal curing under the influence of a catalyst at a temperature ranging from, for instance, about 80°C to about 200°C, depending on the selected polymer.

The powder paint binder composition 15 according to the invention can also be applied in a radiation curable powder paint composition if the modification with, for example, an ethylenically unsaturated group takes place which results in a polymer with vinylether, allyl or propenyl, 20 (meth)acrylate, itaconate, maleate or fumarate functional groups.

A radiation-curable system can comprise for example a resin, a crosslinker, a photoinitiator, a flow agent and pigments.

25 Suitable polymers or crosslinkers which can be added to the radiation curable powder paint compositions according to the invention include for example (meth)acrylated polyesters, (meth)acrylated polyurethanes, (meth)acrylated polyethers, 30 polyepoxides, polyvinylethers, polyallylethers, unsaturated polyesters and poly(meth)acrylates. In this application also a crosslinker comprising units of a

5 prepolymer having a molecular weight (M_n) higher than 400 and units of a vinyl ether or an unsaturated alcohol, the number of polymerizable unsaturations of the crosslinker being higher than or equal to 2, is
very suitable. It is also possible to apply combinations of several polymers and/or crosslinkers.

10 Radiation curing of the binder composition according to the invention preferably takes place through UV and EB curing. These methods are described in more detail in, for instance, the article "UV and
15 EB-curing" by S.J. Bett et al. in JOCCA 1990 (11), pp. 446-453.

15 The compositions according to the invention can be cured by, for example, radical polymerization and by cationic UV polymerization.

20 For the UV radiation curing of a powder paint formulation a photoinitiator can, at a temperature ranging from, for instance, 40°C to 120°C, be mixed with a binder composition according to the invention. A polymer in which the functional, for
25 example, hydroxyl-group is modified into a vinyl ether, allyl or propenyl, (meth)acrylate, itaconate, maleate or fumarate is preferred for this application. An important advantage due to the present invention is the high cure speed, and the possibility of a low temperature curing for example at temperatures lower than 140°C.

30 Mixing can take place both in a solvent and in the melt, for instance in an extruder or in a static mixer. Further, pigments and the desired auxiliary materials such as, for instance, flow agents can be

added. The paint can subsequently be applied to the substrate or be sprayed electrostatically. After application, the powder paint is molten at temperatures ranging from, for instance, 40°C to 170°C by being 5 placed in an oven, exposure to infra-red radiation, or a combination of both, so that a closed, smooth coating film is formed with a layer thickness ranging from, for instance, 20 to 200 µm, after which the still warm panel is cured under a UV light source. Afterwards 10 post-heating may take place.

Examples of suitable photoinitiators are described in Volume 3 "Photoinitiators for free radical and cationic polymerisation" of "Chemistry and Technology of UV and EB formulations" by K. Dietliker 15 (1991; SITA Technology Ltd., London).

Photoinitiators initiate curing of the compositions according to the invention upon exposure to light. Suitable initiators for radical polymerizations are ketonic and may be aromatic such 20 as, for instance, benzophenone. Irgacure 184® (Ciba) is an aryl ketone with hydroxycyclohexyl-phenyl-ketone as active component and is, like Irgacure 369® (active component 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1), a suitable 25 photoinitiator. Acyl phosphine, such as 2,4,6-trimethyl benzoyl diphenyl phosphine oxide (Lucerine TPO®, BASF) can also be used. Chemical derivatives of this photoinitiator are also suitable, as are combinations of these initiators. A suitable combination of 30 photoinitiators is formed by Irgacure 1800® (Ciba),

which consists of 75 wt.% Irgacure 184[®] and 25 wt.% (bis (2,6-dimethoxy benzoyl)-2,4,4-trimethylpentyl phosphine oxide).

The preparation of a powder-paint
5 composition and the chemical curing reactions of
powder-paint compositions into cured coatings are
described in general terms in, for example, Misev,
Powder Coatings, Chemistry and Technology, pp. 44-54,
p. 148 and pp. 225-226, the complete disclosure of
10 which is incorporated herein by reference.

Optionally one or more other
additives suitable for use in paints may also be used.
Examples of suitable additives include pigments,
fillers, degassing agents, flow agents, stabilizers and
15 tribocharging improving agents. Suitable pigments
include for example inorganic pigments, such as
titanium dioxide, zinc sulphide, iron oxide and
chromium oxide, and also organic pigments such as azo
compounds. Suitable fillers include for example metal
20 oxides, silicates, carbonates and sulphates.

Suitable stabilizers include for example
primary and/or secondary antioxidants and UV
stabilizers such as quinones, (sterically hindered)
phenolic compounds, phosphonites, phosphites,
25 thioethers and HALS compounds (hindered amine light
stabilizers).

Examples of degassing agents include
benzoin and cyclohexane dimethanol bisbenzoate.
Examples of flow agents include polyalkylacrylates,
30 fluorohydrocarbons and silicon oils. Suitable additives
are for example additives to improve the tribo-charging
properties, include for example sterically hindered
tertiary amines.

Powder paints according to the invention can be applied to a substrate in the usual manner, for example by means of electrostatic spraying of the powder onto an earthed substrate and curing of the 5 coating such as through exposure to heat at a suitable temperature for a sufficiently long period. The applied powder can for example be heated in a gas oven, an electric oven or with the aid of infrared radiation.

Thermosetting coatings of powder paint 10 (coating) compositions intended for industrial applications are described further in general terms in the already mentioned Powder Coatings by Misev, pp. 141-173 (1991).

Compositions according to the present 15 invention can be used in powder coatings intended for use on for example metal, wood, aluminium, paper, cardboards and plastic substrates. The coatings are also very suitable for use in the automotive industry for coating external and/or internal parts.

20 The invention will be further elucidated with reference to the following, non-limiting examples.

Example I

Preparation of a carboxyl-functional acrylate polymer

25 A mixture consisting of 14.1 g of 2,2'-bipyridine and 288 g of toluene was degassed and inertized with nitrogen. Next, 4.5 g of CuCl was added after which the mixture was heated to 105°C. Next, 15 g of dichloroacetic methyl ester, 31.5 g of methyl 30 methacrylate and 27 g of tert.-butyl acrylate were added. The temperature was kept at 105°C. After 4 hours the tert.-butyl acrylate present had reacted. Next, 210 g of methyl methacrylate was added at 105°C.

Subsequently, after 90% conversion, a mixture consisting of 27 g of tert.-butyl acrylate and 31.5 g of methyl methacrylate was added.

The reaction was continued for another 3 hours to bring about complete conversion. The solution was cooled and filtered. Toluene was removed through distillation and the product obtained, with a molecular weight Mn of 3250, was heated to 200°C, after which the tertiary butyl ester decomposed.

10 The carboxyl-functional polyacrylate obtained had an acid number of 52.4 mg of KOH/g of resin and a glass transition temperature of 92°C.

Example II

15 Preparation of an acrylate polymer

A mixture consisting of 1.562 g of 2,2'bipyridine and 50 g of toluene was degassed and inertized with nitrogen. Next, 0.496 g of CuCl was added, after which the mixture was heated to 105°C. Then 20 3.1 g of dichloroacetic tert-butyl ester and 50 g of methyl methacrylate were added.

The temperature was kept at 105°C. After 90% conversion 2.13 g of tert.-butyl acrylate was added. After 4 hours and 105°C complete conversion was 25 realized. The solution was cooled and filtered. Toluene was removed through distillation and the product, with a molecular weight (Mn) of 3320, was heated to 200°C.

The carboxyl-functional polyacrylate obtained had an acid number of 52.4 mg of KOH/g of 30 resin and a glass transition temperature of 93°C.

Example III

Preparation of a hydroxyl-functional acrylate polymer

940 acrylate polymer obtained according to Example I was dissolved in 500 g of butyl acetate. The solution was heated to 120°C, after which 2 g of catalyst was added. Next, 60 g of propylene oxide was dosed in 2 hours. After additional 3 hours afterreaction at 120°C butyl acetate was removed by vacuum distillation up to 180°C.

10 The polymer obtained had an acid number of <1 mg of KOH/g of resin and a hydroxyl value of 48 mg of KOH/g of resin. The polymer's glass transition temperature was 78°C.

Examples IV-XII15 Powder coatings

16 The polyacrylates obtained according to Examples I-III (Acrylate 1, Acrylate 2 and Acrylate 3, respectively, in Table 2) were mixed with a crosslinker as indicated in Table 2. This mixture was dosed to a kneader at 120°C. After the resin had melted completely, 20 titanium dioxide was dispersed in the resin, after which the other additives were added. After cooling, the product obtained was reduced in size, pulverized and sieved to a maximum particle size of 90 mm. The 25 powder-paint composition was electrostatically applied to an earthed metal substrate and was cured to a powder coating.

26 The curing conditions and properties obtained are shown in Table 3.

30 From this it can be concluded that powder coatings were obtained that possess the desired combination of elasticity, hardness and resistance to chemicals.

Table 2

	IV	V	VI	VII	VIII	IX	X	XI	XII
Acrylate 1	167.3				167.3				
Acrylate 1		155.2				155.2			
Acrylate 1			179.5						
Acrylate 2				167.3					
Acrylate 2					155.2				
Acrylate 3							180	160	
Flexol ¹⁾		32.7			32.7	32.7			
Edenol D82 ²⁾			44.8		44.8	44.8	44.8		
TGIC ³⁾				20.5				20	
Powderlink 1174 ⁴⁾									
Blocked isocyanate ⁵⁾									40
TiO ₂	100	100	100	100	100	100	100	100	100

	IV	V	VI	VII	VIII	IX	X	XI	XII
Resiflow PV5	3	3	3	3	3	3	3	3	3
Benzoin	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
TMG ⁶⁾	1.5	1.5			1.5	1.5	1.5		
DMBA ⁷⁾				0.5					

1) : epoxidized linseed oil (Union Carbide)

2) : epoxidized soybean oil (Henkel)

3) : triglycidyl isocyanurate (CIBA)

4) : tetramethoxymethyl glycoluril (Cyanamid)

5) : tolonate HDT blocked with triazole

6) : tetramethylguanidine

7) : dimethylbenzyl amine

Table 3

	IV	V	VI	VII	VIII	IX	X	XI	XII
Curing time ¹⁾	15'	15'	10'	15'	15'	15'	15'	15'	15'
Hardness ²⁾	192	187	208	180	188	178	190	212	202
Impact resistance ³⁾	60	100	120	80	40	140	100	120	100
ESP ⁴⁾	>8	>8	>8	>8	>8	>8	>8	>8	>8
Acetone rest ⁵⁾	>100	>100	>100	>100	>100	>100	>100	>100	>100

1) : Curing temperature 200°C

2) : König pendulum hardness - DIN 53 157

3) : Reverse impact test - ASTM-2794/69

4) : Erichson slow penetration ISO 1520 - DIN 53156

5) : Acetone double rubs

C L A I M S

1. Powder paint binder composition comprising a A-B-C block polymer formulated from an 5 ethylenically unsaturated monomer, said A block and said C block being terminally disposed and said B block being interposed between said A block and said C block; said A block and said C block having crosslinkable functional groups, said B block being essentially free of reactive functional groups and a crosslinker.
- 10 2. Composition according to Claim 1, characterized in that the combined weight percent of said A block and said C block is less than about 30 wt.% of said A-B-C block polymer.
- 15 3. Composition according to any one of Claims 1-2, characterized in that the polymer is a poly(meth)acrylate or a polystyrene.
4. Composition according to any one of Claims 1-3 20 wherein at least one of the A block and the C block of the A-B-C block polymer is modified into a functional group with a different chemical reactivity (with regard to the starting A-B-C polymer).
- 25 5. Composition according to Claim 4 characterized in that the functional group in the starting A block and/or C block is a hydroxyl group, a carboxylic acid group or an epoxy group and the resulting functional group in the modified A-B-C 30 blockpolymer is a carboxylic acid, an acetoacetate, an alkoxy silane, a vinyl ether, an allyl or propenyl group, a (meth)acrylate, an

itaconate, a maleate or a fumarate, a hydroxyl, an oxazoline, an amide or a carbonate group.

6. A radiation curable powder paint binder composition containing an A-B-C block polymer according to any one of Claims 1-5 in which the functional group in the A and/or C group is modified into a vinyl ether, allyl, propenyl, (meth)acrylate, itaconate, maleate or fumarate group.

10 7. A thermal curable powder paint binder composition containing an A-B-C block polymer according to any of Claims 1-5 in which the functional group in the A and/or C block is modified into a carboxylic acid group.

15 8. Powder paint containing a composition according to any one of Claims 1-7 and optionally pigment, catalyst, filler and additives.

9. Powder coating obtained after curing of a powder paint according to Claim 8.

20 10. Entirely or partly coated substrate, characterized in that a powder coating according to Claim 9 has been used as the coating.

11. A-B-C block polymer formulated from an ethylenically unsaturated monomer, said A block and said C block being terminally disposed and said B block being interposed between said A block and said C block; said A block and said C block having crosslinkable functional groups, said B block being essentially free of reactive functional groups wherein the combined weight percent of said A block and said C block is less than about 30 wt.% of said A-B-C block polymer and

- 30 -

wherein, the polymer is a poly(meth)acrylate or a polystyrene.

13. A-B-C block polymer according to Claim 12 wherein at least one of the A block and the C block is modified into a functional group with a different chemical reactivity (with regard to the starting A-B-C polymer) and wherein the functional group in the starting A block and/or C block is a hydroxyl group, a carboxylic acid group or an epoxy group and the resulting functional group in the modified A-B-C blockpolymer is a carboxylic acid, an acetoacetate, an alkoxysilane, a vinylether, an allyl or propenyl group, a (meth)acrylate, an itaconate, a maleate or fumarate, a hydroxyl, an oxazoline, an amide or a carbonate group.

AMENDED CLAIMS

[received by the International Bureau on 4 October 1999 (04.10.99);
original claims 1-13 replaced by amended claims 1-11 (3 pages)]

1. Powder paint binder composition comprising a A-B-C block polymer formulated from an ethylenically unsaturated monomer, said A block and said C block being terminally disposed and said B block being interposed between said A block and said C block; said A block and said C block having crosslinkable functional groups, said B block being essentially free of reactive functional groups and a crosslinker.
2. Composition according to Claim 1, characterized in that the combined weight percent of said A block and said C block is less than about 30 wt.% of said A-B-C block polymer.
3. Composition according to any one of Claims 1-2, characterized in that the polymer is a poly(meth)acrylate or a polystyrene.
4. Composition according to any one of Claims 1-3 wherein at least one of the A block and the C block of the A-B-C block polymer is modified into a functional group with a different chemical reactivity (with regard to the starting A-B-C polymer).
5. Composition according to Claim 4 characterized in that the functional group in the starting A block and/or C block is a hydroxyl group, a carboxylic acid group or an epoxy group and the resulting functional group in the modified A-B-C block polymer is a carboxylic acid, an acetoacetate, an alkoxysilane, a vinylether, an allyl or propenyl group, a (meth)acrylate, an itaconate, a maleate or a fumarate, a hydroxyl, an oxazoline, an amide or a carbonate group.

6. A radiation curable powder paint binder composition containing an A-B-C block polymer according to any one of Claims 1-5 in which the functional group in the A and/or C group is modified into a vinyl ether, allyl, propenyl, (meth)acrylate, itaconate, maleate or fumarate group.
7. A thermal curable powder paint binder composition containing an A-B-C block polymer according to any of Claims 1-5 in which the functional group in the A and/or C block is modified into a carboxylic acid group.
8. Powder paint containing a composition according to any one of Claims 1-7 and optionally pigment, catalyst, filler and additives.
9. Powder coating obtained after curing of a powder paint according to Claim 8.
10. Entirely or partly coated substrate, characterized in that a powder coating according to Claim 9 has been used as the coating.
11. A-B-C block polymer formulated from an ethylenically unsaturated monomer, said A block and said C block being terminally disposed and said B block being interposed between said A block and said C block; said A block and said C block having crosslinkable functional groups, said B block being essentially free of reactive functional groups wherein the combined weight percent of said A block and said C block is less than about 30 wt.% of said A-B-C block polymer and wherein, the polymer is a poly(meth)acrylate or a polystyrene and wherein at least one of the A block and the C block is modified into a

functional group with a different chemical reactivity (with regard to the starting A-B-C polymer) and wherein the functional group in the starting A block and/or C block is a hydroxyl group, a carboxylic acid group or an epoxy group and the resulting functional group in the modified A-B-C blockpolymer is a carboxylic acid, an acetoacetate, an alkoxysilane, a vinylether, an allyl or propenyl group, a (meth)acrylate, an itaconate, a maleate or fumarate, a hydroxyl, an oxazoline, an amide or a carbonate group.

INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/NL 99/00340A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F293/00 C09D153/00 C09D5/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 260 424 A (COHEN GORDON M ET AL) 9 November 1993 (1993-11-09) claims 1,2 -----	11
A	WO 97 27233 A (BASF AG ;FISCHER MICHAEL (DE); KOCH JUERGEN (DE)) 31 July 1997 (1997-07-31) claim 1 -----	11
A	US 4 925 765 A (MADELEINE DENNIS G) 15 May 1990 (1990-05-15) claims 1,2 -----	11
A	US 5 219 945 A (DICKER IRA B ET AL) 15 June 1993 (1993-06-15) column 3, line 43-52 -----	11

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

24 August 1999

Date of mailing of the international search report

02/09/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Meulemans, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Application No.
PCT/NL 99/00340

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5260424	A 09-11-1993	US 5110869 A		05-05-1992
		AU 612581 B		18-07-1991
		AU 7512887 A		22-12-1987
		AU 626496 B		30-07-1992
		AU 7613991 A		01-08-1991
		DK 42688 A		29-03-1988
		EP 0272285 A		29-06-1988
		JP 1500198 T		26-01-1989
		WO 8707265 A		03-12-1987
		AU 600728 B		23-08-1990
		AU 7348487 A		03-12-1987
		BR 8702725 A		01-03-1988
		CA 1291285 A		22-10-1991
		DK 271587 A		30-11-1987
		EP 0248596 A		09-12-1987
		JP 62290708 A		17-12-1987
		US 4940761 A		10-07-1990
		US 4983679 A		08-01-1992
WO 9727233	A 31-07-1997	DE 19602540 A		31-07-1997
		DE 19626838 A		08-01-1998
		DE 19628834 A		22-01-1998
		AU 1593997 A		20-08-1997
		CN 1209817 A		03-03-1999
		EP 0876414 A		11-11-1998
US 4925765	A 15-05-1990	AU 663464 B		12-10-1995
		AU 4752990 A		01-08-1990
		CA 2006215 A		23-06-1990
		CN 1043801 A		11-07-1990
		DE 68924430 D		02-11-1995
		EP 0457764 A		27-11-1991
		WO 9007732 A		12-07-1990
US 5219945	A 15-06-1993	DE 69312057 D		14-08-1997
		DE 69312057 T		08-01-1998
		EP 0626977 A		07-12-1994
		JP 7503990 T		27-04-1995
		WO 9317057 A		02-09-1993

THIS PAGE BLANK (USPTO)